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(54) **Multifunctional maleate polymers**

Multifunktionale Maleat Polymere

Polymères de maléate multifonctionnelle

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**EP 0 608 845 B1**

**Description**

**[0001]** This invention relates to text of claim 1. Copolymers of maleic acid have unique functional properties that are prepared by an aqueous solution process to yields a copolymer comprising at least 50 mole percent maleate and less than 1%, on a copolymer weight basis, residual free monomer. The process used to prepare this copolymer is carried out in the presence of a redox catalyst system, comprising at least one initiator and appropriate metallic ions, with slow feed addition of the comonomer(s), together with the post-addition of initiator. The maleate copolymers are useful in a variety of applications requiring modification of salt crystal formation in aqueous solution.

**[0002]** It is known that maleic acid and maleic anhydride monomers do not readily form homopolymers, but will quite rapidly copolymerize with various other ethylenically unsaturated monomers, typically to form 1:1 molar ratio maleate:comonomer copolymers.

**[0003]** In most cases, maleate copolymers are prepared by a solution polymerization process employing organic solvents. For example, U.S. Patent No. 4,710,537, issued December 1, 1987 to Walinsky, teaches the preparation of a substantially homogeneous copolymer, consisting essentially of 35 to 65 mole percent acrylate and 65 to 35 mole percent maleate units and having a number average molecular weight of about 500 to 5,000. The copolymer is prepared in a chain-transfer solvent, preferably a ketone, ester, or ether having from 4 to 10 carbon atoms. Following polymerization, an aqueous solution of the copolymer may be prepared by adding water to the polymerization flask and distilling off the organic solvent.

**[0004]** For reasons of safety, efficiency in manufacturing and waste handling, it is desirable to polymerize the maleate copolymers in aqueous solution, rather than in organic solvent. An aqueous solution preparation of maleate copolymers is disclosed in JP -A-60-212,410, published October 24, 1985 by Fukumoto, et al. The polymerization method provides maleate copolymers with mean molecular weights of 300 to 5,000 and has a reported "polymerization rate" of, at most, 96.2%. The "polymerization rate" is the difference between the weight of monomer initially charged and the weight of copolymer recovered following polymerization (i.e., a measure of the unreacted residual monomer).

**[0005]** Another method for preparation of maleate copolymers in aqueous solution is disclosed in U.S. -A-4,519,920, issued May 28, 1985, to Fukumoto, et al. This process provides an initial, partial neutralization of the maleate monomer with alkali. A similar aqueous solution process for producing a polymaleate, with an option to copolymerize up to 20 mole percent of an unsaturated carboxylic acid comonomer, is disclosed in U.S. -A-4,668,735, issued May 26, 1987, to Fukumoto, et al.

**[0006]** U.S. -A-3,635,915, issued January 18, 1972 to Gale, discloses a process for preparing maleate/acrylate copolymers in aqueous solution using an inorganic peracid salt as a catalyst. The copolymers are prepared from 50 to 95 parts of acrylic acid and 5 to 50 parts of maleic acid, on a monomer weight basis (i.e., 57.5 to 96.5 mole percent acrylate and 3.5 to 42.5 mole percent maleate).

**[0007]** U.S. -A-4,659,793, issued April 21, 1987, to Yang claims an aqueous polymerization process for manufacturing copolymer having a low residual free monomer content from carboxylic acid monomers and various comonomers. In the claimed process a metallic ion redox catalyst is used to prepare a copolymer comprising 25 to 55 weight percent (i.e., 21 to 47 mole percent) dicarboxylic acid monomer.

**[0008]** Further, there is disclosed a maleate copolymer having a weight average molecular weight of 2,000 to 1,000,000, a residual total monomer content of less than 0.5% on a maleate copolymer dry weight basis, and comprising of 10 to 70% of maleate, 10 to 50% of acrylate monomer and not more than 30% vinyl monomers selected from acrylamide, N,N'-dimethylacrylamide, hydroxy ethyl acrylate, hydroxypropylacrylate, vinyl-pyrrolidone and vinyl acetate. Such copolymers are used as antiscalants, dispersants and detergent additives.

**[0009]** U.S. -A-4,314,044, issued February 2, 1982 to Hughes, et al., claims an aqueous polymerization process for manufacturing copolymers of carboxylic acid monomers using a metallic ion redox catalyst system. As exemplified in the patent, the process only achieves about 95% monomer conversion. About 5 to 50 weight percent dicarboxylic acid is polymerized in the claimed process.

**[0010]** The processes for preparing maleate polymers and copolymers known in the art disadvantageously result in unacceptable levels of free, residual monomer, in particular, free, residual maleate monomer in the product of the Polymerization. Such free, residual monomer is undesirable in many end use applications, particularly applications relating to personal care products, detergents and cleaners as well as industrial end uses involving further chemical reactions in which the residual monomer may participate as an undesirable reactant.

**[0011]** We have now discovered that an aqueous solution polymerization, employing a combination of at least 70 mole percent charge preneutralization of the maleate monomer, a redox initiator catalyst using metallic ion, a slow feed addition of at least one comonomer, preferably over a period of at least three hours, to the neutralized maleate monomer and a post-feed of a polymerization initiator provides a copolymer having a weight average molecular weight of about 500 to 7,000, comprising at least 50 mole percent maleate, and less than 1%, on a copolymer weight basis, of residual, free monomer. This process may be carried out under ambient atmospheric conditions. An inert atmosphere, such as nitrogen, is not required for the polymerization. The resulting copolymer is useful as an antiscalant, an anti-incrustation

agent, a dispersant, a detergent adjunct, a sequestrant and a water hardness salt (e.g., calcium carbonate, magnesium carbonate, magnesium sulfate, magnesium hydroxide, calcium sulfate and barium sulfate) crystal modifier.

**[0012]** The processes claimed herein include processes for dispersing clay, salts, pigments and ores in aqueous slurries used in pulp and paper manufacturing and in drilling, mining and manufacturing operations each utilizing the maleate copolymer of this invention.

**[0013]** The maleate copolymer comprises at least 50 mole percent maleate, 10 to 50 mole percent acrylic or methacrylic acid and 1 to 10 mole percent and less than 1%, preferably less than 0.25%, by weight, residual total monomer content whereby the proportions of the constituents add up to 100 mole-%. The maleate copolymer has a weight average molecular weight of about 500 to 7,000, preferably 2,000 to 4,000.

**[0014]** The maleate copolymers having unique functional properties are prepared by an aqueous solution polymerization process. At least 70%, on a mole charge basis, of the charged groups of the maleate monomer are preneutralized with alkali. An effective amount (e.g., 1-4 ppm), on a total batch weight basis, metallic ions suitable for use as a reductant in a redox catalyst is added to the preneutralized maleate monomer. A monocarboxylic acid monomer, and at least one initiator, and a third nonionic comonomer, and, optionally, additional alkali, are slowly added to the neutralized maleate over at least a three hour period at 80-180°C. Following a post-addition of more initiator, preferably to provide a total of at least 4% initiator, on a total monomer mole basis, the aqueous solution of the maleate copolymer comprises less than 1%, by weight, free, residual monomer and the copolymer has a weight average molecular weight of about 500 to 7,000.

**[0015]** In the process for preparing the copolymers of this invention an aqueous solution, comprising 20 to 35%, preferably comprising 27 to 30%, by weight, of maleate monomer is prepared. Suitable maleate monomers include maleic acid, maleic anhydride, alkali metal maleate salts, ammonium maleate salts, and mixtures thereof.

**[0016]** In the initial step of the process, the aqueous maleate solution is neutralized by the addition of alkali. Each mole of maleate comprises two moles of carboxylic acid charge. Thus, two moles of alkali are required for each mole of maleate monomer to provide 100% charge neutralization of the monomer. For the purposes of this invention, at least 70% of the carboxylic acid charge, preferably at least 80%, must be neutralized prior to polymerization.

**[0017]** Any base may be used for this step. In a preferred embodiment, an aqueous solution of an alkali metal hydroxide, such as sodium or potassium hydroxide or an aqueous ammonium solution is added to the maleate monomer solution.

**[0018]** The polymerization is carried out at 80 to 180°C, preferably 90 to 100°C, and most preferably, 95 to 100°C, under reflux. If the temperature is permitted to remain below 90°C, the neutralized maleate salt is likely to precipitate out of the reaction solution. If a relatively labile comonomer, such as acrylamide, is used, then monomer will be lost at temperatures exceeding 100°C and it is preferred to maintain the temperature below 100°C. The reflux may be carried out under ambient atmosphere or under inert atmosphere, such as nitrogen. Likewise, the reaction may be carried out under greater than atmospheric pressure (e.g., ½ to 1½ atmospheres), although ordinary atmospheric conditions are suitable and are preferred.

**[0019]** The process employs as a polymerization initiator at least one redox catalyst, comprising at least one initiator and at least one metallic ion suitable for use as a reductant in a redox catalyst system. Such reducible cations include the metallic ions obtained from iron, zinc, cobalt, molybdenum, chromium, nickel, vanadium and cerium, and combinations thereof. Preferred metallic ions are obtained from ferrous ammonium sulfate, ferrous sulfate, ferrous chloride, cobalt salts (e.g., cobalt sulfate hexahydrate), vanadium salts, and combinations thereof, and other water soluble salts producing metallic ions that are susceptible to oxidation by oxidants typically used in redox catalysts as polymerization initiators. Such initiators include hydrogen peroxide, benzoyl peroxide, sodium persulfate and sodium persulfate bisulfite, t-butyl hydroperoxide, cumene hydroperoxide, dialkyl peroxide, ammonium persulfate and ammonium persulfate/bisulfite, and combinations thereof. A mixture of initiators is preferred. The initiator is preferably utilized at about 4 to 15%, on a total monomer mole basis, together with an effective amount of metallic ion, preferably at least 1 ppm, most preferably at least 4 ppm metallic ion, on a total batch weight basis. The initiator and metallic ion may be added to the initial maleate charge, or added with the feed of the comonomer(s), or both. A reductant, such as erythorbic acid or ascorbic acid is preferably added after polymerization. A post-polymerization addition of initiator is an essential aspect of this invention.

**[0020]** In a preferred embodiment an initiator comprising, on a total monomer weight basis, 10 to 15% hydrogen peroxide and 4 to 6% sodium persulfate is added along with the comonomer(s) feed. A total of 7 to 40 ppm ferrous ammonium sulfate hexahydrate is added to the initial maleate charge. A total of 1 to 2% hydrogen peroxide and 0.25 to 0.35% sodium persulfate is added during the post-polymerization period.

**[0021]** The comonomer(s), either in aqueous solution or neat, are added slowly during polymerization over a period from about 3 to 10 hours. In a preferred embodiment, the comonomer(s) are partially neutralized by adding the comonomer(s) to an aqueous solution of alkali prior to addition to the polymerization flask. In the alternative, alkali may be added simultaneously with the comonomer(s) to regulate reaction pH.

**[0022]** Suitable comonomers include ethylenically unsaturated monocarboxylic acids, preferably acrylic acid, and,

optionally, other copolymerizable comonomers. Preferred monocarboxylic acid monomers include acrylic acid, methacrylic acid and ethacrylic acid, and combinations thereof (the "acrylate" monomer). The acrylate monomers useful in the production of the polymers of this invention are the olefinically unsaturated carboxylic acids containing at least one activated carbon-to-carbon olefinic double bond, and at least one carboxyl group, that is, an acid containing an olefinic double bond which readily functions in polymerization because of its presence in the monomer molecule either in the alpha-beta position with respect to a carboxyl group, or as a part of a terminal methylene grouping.

**[0023]** In a preferred copolymer of this invention, the copolymer comprises at least one comonomer in addition to the maleate and acrylate monomers. Useful olefinically-unsaturated acids of this class include such widely divergent materials as the acrylic acid comonomers typified by acrylic acid itself, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, alpha-cyano acrylic acid, beta methyl-acrylic acid (crotonic acid), alpha-phenyl acrylic acid, beta-acryloxy propionic acid, sorbic acid, alpha-chloro sorbic acid, angelic acid, cinnamic acid, p-chloro cinnamic acid, beta-styryl acrylic acid (1-carboxy-4-phenyl butadiene-1,3), itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, fumaric acid, and tricarboxy ethylene. For the polycarboxylic acid monomers, an anhydride group is formed by the elimination of one molecule of water from two carboxyl groups located on the same polycarboxylic acid molecule.

The preferred carboxylic monomers for use in this invention are the monoolefinic acrylic acids having a substituent selected from the class consisting of hydrogen, halogen and hydroxyl groups, monovalent alkyl radicals, monovalent aryl radicals, monovalent aralkyl radicals, monovalent alkaryl radicals and monovalent cycloaliphatic radicals.

**[0024]** Other suitable optional comonomers for preparing the copolymers herein include any water-soluble, unsaturated compounds that are capable of free radical polymerization utilizing a redox catalyst.

**[0025]** Water soluble is defined herein to mean comonomers which have a minimum solubility of 5% by weight in water at 25°C. Such comonomers include acrylic and methacrylic acid (the "acrylate" monomer group); acrylamide, methacrylamide, acrylonitrile; N,N-dialkylaminoalkyl acrylates and methacrylates (wherein the alkyl group contains 1 to 4 carbon atoms); ethylenically unsaturated quaternary ammonium salts such as N,N,N-trimethylaminoethyl methacrylate methylsulfate or halide, 2-hydroxy-3-methacryloxypropyltrimethyl-ammonium methyl sulfate or halide, vinylbenzyltrialkylammonium methylsulfate or halide; sodium or ammonium styrenesulfonate; vinyl pyrrolidinone; hydroxyl alkyl acrylates and methacrylates; sodium 2-acrylamide-2-methylpropane sulfonate, etc. Various other water-soluble comonomers suitable for polymerization with maleate and acrylate monomers are known to those skilled in the art.

**[0026]** The maleate monomer is present in the copolymers of this invention at a mole ratio of least 50%. The second carboxylic acid monomer, preferably acrylic acid monomer, is present in the copolymer of this invention at a mole ratio of 10 to 50%. The copolymer further comprises at least one additional non-ionic comonomer, exemplified by acrylamide, N-vinyl-2-pyrrolidinone, diallylamine, hydroxypropylacrylate, hydroxyethylacrylate and vinyl acetate. The copolymer comprises at least 50 mole percent maleate, 10 to 50 mole percent acrylate and 1 to 10 mole percent non-ionic comonomer.

**[0027]** The copolymers prepared by the process of this invention preferably have a weight average molecular weight of 500 to 7000. In a preferred embodiment, the copolymers have a molecular weight of 1000 to 4000, most preferably 2000 to 4000.

**[0028]** The copolymers of this invention are characterized by an extremely low residual monomer content of less than about 1%, on a dry copolymer weight basis. In a preferred embodiment, the copolymers of this invention comprise no more than 0.25% residual monomer, on a copolymer dry weight basis. The percent residual monomer calculations are based on maleate monomer.

**[0029]** The copolymers of maleate/acrylate/comonomer comprising at least 50 mole percent maleate and having a weight average molecular weight of 500 to 7,000 and less than 1%, on a copolymer weight basis, residual monomer, exhibit unique functional characteristics in various end use applications.

**[0030]** The maleate copolymers may be used as dispersants in industrial applications to provide stable aqueous dispersions or slurries of pigments, clays, salts, metallic ores and oxides in a variety of manufacturing operations. As a dispersant, the maleate copolymer is typically effective at a usage level of 0.05 to 2.0%, preferably 0.05 to 0.5%, on a solids weight basis.

**[0031]** In particular, the maleate copolymers may be used to disperse solids (e.g. clay, pigments) in wood pulp aqueous slurries and in other aqueous systems used in the manufacture of paper.

#### **EXAMPLE 1**

**[0032]** This example illustrates the process for preparing the copolymers of this invention.

**[0033]** Synthesis of the copolymers is described in Parts A - E, below. Copolymer characteristics are described in Table I, below.

Table I

Copolymer Synthesis						
Copolymer Sample	Monomer <sup>a</sup> Molar Ratio	Degree of Pre-Neutralization of Maleate (mole %)	Final pH	Mw	Mn	Percent Residual Monomer <sup>b</sup>
Part A						
1	MA/AA/AM 50/45/5	70	5.2	2522	1805	<0.01
2	MA/AA 60/40	80	5.7	2297	1555	0.1
3	MA/AA 50/50	50	6.3	2672	1254	<0.01
Part B						
4	MA/AA/AM 50/40/10	75	5.2	2367	1755	0.03
5	MA/AA/AM 50/42/8	85	5.7	2203	1653	<0.1
6	MA/AA/AM 60/35/15	85	5.8	1786	1113	0.18
7	MA/AA/AM 50/49/1	80	4.9	2700	1906	<0.01
8	MA/AA/AM 50/35/15	80	5.6	2830	1909	0.07
Part C						
9	MA/AA/VP 50/45/5	80	5.0	2639	1873	<0.1
10	MA/AA/DA 50/45/5	80	5.2	2990	1876	<0.1
11	MA/AA/HPA 50/45/5	80	5.1	2698	1727	<0.1
12	MA/AA/HEA 50/45/5	80	5.1	2652	1851	<0.1
13	MA/AA/AM 50/45/5	80	5.4	3063	2028	<0.1
Part D						
14	MA/AA/VA 50/45/5	80	4.8	3246	2092	<0.01
15	MA/AM 70/30	50	5.8	2698	1643	<0.01
Part E						
16	MA/AA 67/33	52.5	-	3600	-	2.1 (precipitated) <sup>c</sup>
Part F						
17	MA/AA 67/33	52.5	5.2	3094	1938	0.40

a. MA is maleic acid or anhydride; AA is acrylic acid; AM is acrylamide; VP is N-vinyl-2-pyrrolidinone; DA is diallylamine; HPA is hydroxypropylacrylate; HEA is hydroxyethylacrylate; and VA is vinyl acetate.

b. For samples 9-13, monomer content was measured by gel permeation chromatography following polymerization. All other samples were measured using a liquid chromatograph.

c. The residual monomer was present in sufficient quantity to precipitate from the polymerization solution. The precipitate was redissolved and analyzed by liquid chromatography. No final pH nor  $M_n$  measurements were made.

#### Part A

**[0034]** Copolymer 1 (50/45/5 maleic/acrylic/acrylamide): A charge of 2.47 moles (242.0 grams) maleic anhydride in 350 grams of deionized water was placed into a flask equipped with two dropping funnels, a reflux condenser, a nitrogen

inlet and a stirrer. The maleic anhydride was 70% neutralized by the addition of 276.6 grams of 50% sodium hydroxide solution (0.7 mole of base/mole of carboxylic acid charge of the maleate monomer, or 1.4 moles base/mole of maleate monomer). Based on monomer weight, 10.6 ppm ferrous ions (0.03 grams of ferrous ammonium sulfate hexahydrate), and 1.0 g ascorbic acid were added to the flask.

5 [0035] At a reflux temperature of 98-100°C, a feed containing 2.23 moles (160.6 grams) of acrylic acid and 0.25 moles acrylamide (34.0 g of a 52% aqueous solution) and 30.0 g of a 50% solution of sodium hydroxide in 130.0 grams of deionized water, and a second feed containing 11.8% (142 g) of hydrogen peroxide and 4.3% sodium persulfate (18 g in 104.5 water), on a total monomer weight basis, were added drop wise, with stirring, to the flask over a 5 hour, 15 minute period followed by a two hour cook.

10 [0036] Total solids, pH and intrinsic viscosity in 1N NaCl were recorded. The molecular weight was measured by gel permeation chromatography using polyacrylate standards. The residual monomer (a total of maleic acid, acrylic acid and fumaric acid) was measured by liquid chromatography using a Waters Liquid Chromatograph apparatus.

[0037] Copolymer 2 (67/33 maleic/acrylic): A copolymer was synthesized as described above except: (1) 1.32 moles of maleic anhydride (129.4 grams) and 0.66 moles of acrylic acid (47.5 grams) were used, (2) the initiator charge comprised 10.8% hydrogen peroxide and 4.5% sodium persulfate, on a total monomer mole basis, (3) 5 ppm (on a total batch weight basis) ferrous ammonium sulfate hexahydrate, was added to the maleate monomer, (4) the feed time was 5 hours followed by a 20 minute initiator post feed and (5) a post treatment of 0.17%, on a monomer weight basis, of erythorbic acid was added to the aqueous copolymer.

15 [0038] Copolymer 3 (50/50 maleic/acrylic): A copolymer was synthesized as described above, except: (1) a charge of 2.57 moles of maleic anhydride (251.5 g) in 400 g of deionized water 0.118 g ferrous ammonium sulfate hexahydrate, 150 g isopropanol, and 209.5 g of a 50% solution of sodium hydroxide, and a feed of 2.57 moles acrylic acid (184.8 g) and 104.4 g of a 50% solution of sodium hydroxide in 140.1 g of deionized water were used, (2), the maleate was 50% neutralized with base prior to polymerization, (3) comonomer feed was added over a 5 hour period, and an additional initiator (168.5 g of a 35% solution of hydrogen peroxide) feed was added simultaneously over a 6 hour period. 25 Following the synthesis, 85 g of a 50% sodium hydroxide solution, was added to the flask and the copolymer was recovered in aqueous solution following distillation to remove isopropanol.

## Part B

30 [0039] Copolymers 4-8 (maleic/acrylic/acryl-amide): Copolymers were synthesized as described above except that the molar ratio of the monomers was varied.

[0040] Copolymer 4 was prepared from a molar ratio of 50/40/10 maleic/acrylic/acrylamide, using 2.57 moles maleic anhydride (251.9 g), 2.06 moles acrylic acid (148.3 g) and 0.51 moles acrylamide (69.6 g of a 52% solution). The initial charge included the maleate, 400.0 g of deionized water, 308.4 g of a 50% sodium hydroxide solution, 150.0 g isopropanol, 0.118 g of ferrous ammonium sulfate hexahydrate and 2.5 g of a 35% solution of hydrogen peroxide. The monomer feed contained 150.0 g of deionized water in addition to the acrylic acid and acrylamide. The initiator feed contained 183.0 g of hydrogen peroxide in 100.0 g of deionized water. Following synthesis, 250.0 g of 50% sodium hydroxide was added.

35 [0041] Copolymer 5 was prepared from a molar ratio of 50/42/8 maleic/acrylic/acrylamide, using 2.57 moles maleic anhydride (251.9 g), 2.14 moles acrylic acid (154.0 g, glacial) and 0.43 moles acrylamide (58.7 g, 52% solution). The initial charge contained the maleic anhydride, 362 g deionized water 349.5 g of 50% sodium hydroxide, and an initiator mixture of 0.03 g ferrous ammonium sulfate hexahydrate and 3.0 g of erythorbic acid. The monomer feed contained the acrylic acid, acrylamide, 20.0 g of 50% sodium hydroxide and 175.0 g of deionized water. The initiator feed contained 1.42 moles of hydrogen peroxide (138.0 g of a 35% solution) and 0.122 moles of sodium persulfate (29 g in 116.5 g of deionized water). The monomer was added over 5 hours, the initiator over 5 hours and 15 minutes and synthesis was followed by a 2 hour cook.

40 [0042] Copolymer 6 was prepared from a molar ratio of 60/35/5 maleic/acrylic/acrylamide, using 3.08 moles maleic anhydride (301.8 g), 1.80 moles acrylic acid (129.6 g, glacial) and 0.25 moles acrylamide (34.2 g, 52% solution). The initial charge contained the same components as in copolymer 5 except sodium hydroxide was increased to 418.8 g and the water to 385.0 g. The monomer feed contained the monomers in 15.0 g of 50% sodium hydroxide and 120.0 g of water. The initiator feed contained 150.0 g of 35% hydrogen peroxide, and 35.0 g of sodium persulfate in 120.0 g of water.

45 [0043] Copolymer 7 was prepared from a molar ratio of 50/49/1 maleic/acrylic/acrylamide, using 1.23 moles maleic anhydride (121 g), 1.21 moles acrylic acid (87.1 g, glacial) and 0.025 moles acrylamide (3.5 g, 50% solution). The initial charge contained maleic anhydride, 175 g deionized water 158 g 50% sodium hydroxide, and 0.02 g of ferrous ammonium sulfate hexahydrate. The monomer feed contained 64.5 g of 35% hydrogen peroxide, and 9.5 g of sodium persulfate in 10 g deionized water.

[0044] Copolymer 8 was prepared from a molar ratio of 50/35/15 maleic/acrylic/acrylamide, using 1.23 moles maleic

anhydride, (121 g), 0.863 moles acrylic acid (62.1 g, glacial) and 0.37 moles acrylamide (52.5 g of 50% solution). The initial charge contained the same components as Copolymer 7. The monomer feed contained the monomers in 45.0 g of deionized water. The initiator feed was the same as Copolymer 7.

### Part C

[0045] Copolymers 9-14 (maleic/acrylic 50/45 and 5% third monomer): Copolymers 9-14 were synthesized as described above for copolymer 3, except that various non-ionic monomers were substituted for acrylamide at 5 mole percent. The third monomers tested included, N-vinyl-pyrrolidone, diallylamine, hydroxypropyl acrylate, hydroxyethyl acrylate, vinyl acetate and acrylamide (control).

### Part D

[0046] For comparative purposes, copolymer 15, a copolymer of maleic acid and acrylamide in a molar ratio of 70/30 was synthesized as described for copolymer 3, above, except no acrylic acid was used.

### Part E

[0047] For comparative purposes, copolymer 16, a copolymer of maleic and acrylic acids in 67/33 molar ratio, was synthesized as described in Example 1 of U.S. Pat. No. 4,519,920 (the "Kao '920 patent"). In the Kao '920 synthesis, the initial maleate charge was only 52.5% neutralized with sodium hydroxide (a molar ratio of maleic anhydride/sodium hydroxide of 1.00/1.05). The Kao '920 synthesis also differed from the synthesis of copolymer 2 of this invention in that an additional 5.0% sodium hydroxide was added with the acrylic acid, only 9.55%, on a total monomer molar basis, of a single initiator (hydrogen peroxide) was used, and there was no initiator post-feed.

### Part F

[0048] For comparative purposes, copolymer 17, a copolymer of maleic and acrylic acids in 67/33 molar ratio, was synthesized as described for copolymer 2, above, except the maleic anhydride was 52.5% pre-neutralized and the initiator charge was increased to 15.5%, on a total monomer weight basis.

## EXAMPLE 2

[0049] This example illustrates the utility of the copolymers of this invention as clay dispersants.

[0050] An acid washed Kaolin clay slurry was used for comparing experimental copolymers to control polymers (commercially used) as dispersants. The treated clay slurries were tested for Brookfield (low shear) and Hercules (high shear) viscosities and two week stability at elevated temperature (50°C). The amount of copolymer used to disperse the clay in aqueous slurry was adjusted to give approximately the same initial viscosity in the slurry. Results are shown in Table VII, below.

Table VII

Clay Dispersant Test							
Sample <sup>a</sup> (mol. wt.)	Lbs/ton (Optimum Level) <sup>b</sup>	Brookfield 20 rpm	Sp	pH	Hercules <sup>c</sup> Bob A 1100 rpm (offscale)	After 2 wks @50°C Brookfield 20 rpm	
						unstirred	stirred
Control Polyacrylic Acid (2,500-2,700)	3.0	266	1	7.0	740 rpm	1440	650

a. Copolymers are described in Example 1, above. The monomer, 2-acrylamide-2-methylpropane sulfonate, was obtained from Lubrizol Corporation, and is sold under the AMPS® trademark.

b. The amount of polymer added to the clay was adjusted to give the optimum product viscosity for a 70% solids clay slurry.

c. The Hercules end point for shear viscosity at 1100 rpm was measured using a Bob A spindle.

Table VII (continued)

Clay Dispersant Test							
Sample <sup>a</sup> (mol. wt.)	Lbs/ton (Optimum Level) <sup>b</sup>	Brookfield 20 rpm	Sp	pH	Hercules <sup>c</sup> Bob A 1100 rpm (offscale)	After 2 wks @ 50°C Brookfield 20 rpm	
						unstirred	stirred
Control Acrylic Acid/ AMPS® Copolymer (≤ 3,000)	2.5	246	1	7.1	905 rpm	1560	440
Copolymer -13	4.0	260	1	6.6	695 rpm	1640	520
Copolymer 1	4.5	256	1	6.6	735 rpm	1060	450

a. Copolymers are described in Example 1, above. The monomer, 2-acrylamide-2-methylpropane sulfonate, was obtained from Lubrizol Corporation, and is sold under the AMPS® trademark.

b. The amount of polymer added to the clay was adjusted to give the optimum product viscosity for a 70% solids clay slurry.

c. The Hercules end point for shear viscosity at 1100 rpm was measured using a Bob A spindle.

[0051] The results show that although larger amounts of experimental polymer were required, the experimental polymer gave viscosity profiles and storage characteristics similar to those of the commercially used control polymers. Thus, the copolymers of this invention are useful as clay dispersants.

#### Claims

1. A process for dispersing pigments, clays, salts, metallic ores and oxides in an aqueous slurry, comprising the step of adding to the aqueous slurry an effective amount of a maleate copolymer having a weight average molecular weight of 500 to 7,000, a residual total monomer content of less than 1%, on a maleate copolymer dry weight basis, and comprising at least 50 mole percent of maleate monomer and 10 to 50 mole percent of acrylate monomer, and 1 to 10 mole percent of at least one nonionic monomer selected from the group of consisting of acrylamide, metacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N,N-dipropylacrylamide, vinylacetate, N-vinyl-2-pyrrolidone, diallylamine, hydroxypropylacrylate and hydroxyethylacrylate, whereby the proportions of the constituents add up to 100 mole-%, wherein a stable aqueous dispersion of the pigments, clays, salts, and metallic ores and oxides is created by adding the maleate copolymer, wherein prior to the polymerization at least 70 mole percent of the maleate monomer are neutralised.
2. The process of Claim 1, wherein the maleate copolymer has an average molecular weight of 2,000 to 4,000.
3. The process of Claim 1, wherein the maleate copolymer is prepared by an aqueous solution polymerization process.

#### Patentansprüche

1. Verfahren zum Dispergieren von Pigmenten, Ton, Salzen, metallischen Kernen und Oxiden in einer wäßrigen Aufschlämmung, umfassend die Stufe Zusetzen zu der wäßrigen Aufschlämmung eine wirksame Menge eines Maleatcopolymers, das ein Gewichtsmittel des Molekulargewichts von 500 bis 7000, einen restlichen Gesamtmonomergehalt von weniger als 1 %, bezogen auf das Maleatcopolymer-Trockengewicht als Basis, hat und das mindestens 50 mol-% Maleatmonomer und 10 bis 50 mol-% Acrylatmonomer und 1 bis 10 mol-% mindestens



eines nicht-ionischen Monomeren, ausgewählt aus der Gruppe, bestehend aus Acrylamid, Methacrylamid, N,N-Dimethylacrylamid, N,N-Diethylacrylamid, N,N-Dipropylacrylamid, Vinylacetat, N-Vinyl-2-pyrrolidon, Diallylamin, Hydroxypropylacrylat und Hydroxyethylacrylat umfaßt, wobei die Anteile der Bestandteile sich zu 100 mol-% addieren, wobei durch Zusetzen des Maleatcopolymeren eine stabile wäßrige Dispersion der Pigmente, von Ton, Salzen und metallischen Kernen und Oxiden gebildet wird und vor der Polymerisation mindestens 70 mol-% des Maleatmonomeren neutralisiert werden.

2. Verfahren nach Anspruch 1, wobei das Maleatcopolymer ein durchschnittliches Molekulargewicht von 2000 bis 4000 hat.
3. Verfahren nach Anspruch 1, wobei das Maleatcopolymer durch Polymerisationsverfahren in wäßriger Lösung hergestellt wird.

## Revendications

1. Procédé pour disperser des pigments, des argiles, des sels, des minerais métalliques et oxydes dans une suspension aqueuse, comprenant l'étape consistant à ajouter à la suspension aqueuse une quantité efficace d'un copolymère de maléate ayant une moyenne en poids du poids moléculaire de 500 à 7000, une teneur en monomères totaux résiduels inférieure à 1 %, sur la base du poids sec du copolymère de maléate, et comprenant au moins 50 pour cent en mole de monomère maléate et 10 à 50 pour cent en mole de monomère acrylate, et 1 à 10 pour cent en mole d'au moins un monomère non ionique choisi dans le groupe consistant en l'acrylamide, le méthacrylamide, le N,N-diméthylacrylamide, le N,N-diéthylacrylamide, le N,N-dipropylacrylamide, l'acétate de vinyle, la N-vinyl-2-pyrrolidone, la diallylamine, l'acrylate d'hydroxypropyle et l'acrylate d'hydroxyéthyle, les proportions des constituants ajoutés atteignant ainsi 100 % en moles, dans lequel une dispersion aqueuse stable des pigments, argiles, sels et minerais métalliques et oxydes est formée en ajoutant le copolymère de maléate, et dans lequel, avant la polymérisation, une quantité d'au moins 70 pour cent en mole du monomère de maléate est neutralisée.
2. Procédé suivant la revendication 1, dans lequel le copolymère de maléate a un poids moléculaire moyen de 2000 à 4000.
3. Procédé suivant la revendication 1, dans lequel le copolymère de maléate est préparé par un procédé de polymérisation en solution aqueuse.